

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-307124

(43)Date of publication of application : 05.11.1999

(51)Int.Cl.

H01M 10/40  
H01M 4/02

(21)Application number : 10-108029

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(22)Date of filing : 17.04.1998

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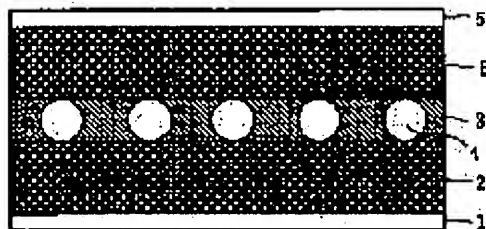
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## (54) SECONDARY BATTERY AND ITS MANUFACTURE

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a secondary battery that can precisely control the distance between both electrodes without using a separator which does not contribute to ion conductivity, as is conventionally done, obviates the need of the consideration on liquid leakage, and can provide battery performance equivalent to a lithium ion second battery using a conventional liquid electrolyte.

**SOLUTION:** This secondary battery has a structure provided with: a positive electrode composed by forming a positive electrode active material layer 2 on a positive electrode collector 1; a negative electrode composed by forming a negative electrode active material layer 6 on a negative electrode collector 5; and an ion conductive layer 3 formed from a nonfluidic ion conductive composition containing spacer particles 4, between the positive electrode active material layer 2 and the negative electrode active material layer 6, to control the distance between the positive electrode active material layer 2 and the negative electrode active material layer 6.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a rechargeable battery and its manufacture approach. It is related with the ionic conduction layer of a rechargeable battery in more detail.

[0002]

[Description of the Prior Art] The request to small and lightweight-izing of pocket electronic equipment is very large. It depends for the implementation on the improvement in the engine performance of a cell greatly, and development of various cells and amelioration have been advanced that it should correspond to this. The property required of a cell has the high voltage, a high energy consistency, safety, the optionality of a configuration, etc. A rechargeable lithium-ion battery is a rechargeable battery with which it is expected that the high voltage and a high energy consistency will be most realized also in an old cell, and the amelioration is briskly advanced even for current.

[0003] A rechargeable lithium-ion battery has the ionic conduction layer pinched by a positive electrode and a negative electrode, and this positive electrode and negative electrode as that main component. In the rechargeable lithium-ion battery with which current practical use is presented, what applied to the charge collector the positive active material which consists of powder, such as a lithium-cobalt multiple oxide, and was made tabular is used for a positive electrode, and what applied to the charge collector the negative-electrode active material which consists of powder of a carbon system ingredient, and was made tabular is used for the negative electrode. Moreover, what filled the electrolytic solution of a non-drainage system on porosity films, such as polypropylene, is used for the ionic conduction layer.

[0004] It is required that an ionic conduction layer should require that there should be no electronic conduction nature, and cell engine-performance top ionic conduction resistance should be low. That is, if resistance of an ionic conduction layer is made low, the charge and discharge in a high current will become more possible. On the other hand, it is required that two electrodes should be separated in a predetermined distance through an ionic conduction layer so that between two electrodes (a positive electrode and negative electrode) may not connect too hastily. It becomes the important point to separate two electrodes in a predetermined distance from a viewpoint of obtaining the cell engine performance by which the short circuit was prevented and stabilized.

[0005] The rechargeable lithium-ion battery with which current practical use is presented separates two electrodes with this separator as mentioned above using the separator which consists of a porosity film, and enables migration of the ion between two electrodes by being filled up with the electrolytic solution which bears ionic conduction between two electrodes further. Moreover, in order to maintain the electric contact to two electrodes and a separator, the structure which consists of a separator inserted into firm sheathing cans, such as a metal, between two electrodes and these two electrodes is contained, and it is made the structure which puts a pressure on this structure from the exterior. The technique about a rechargeable lithium-ion battery with such structure is indicated by JP,8-83608,A.

[0006] Since the rechargeable lithium-ion battery constituted as mentioned above has connoted the electrolytic solution, the consideration to the leakage of the electrolytic solution is needed. Then, it

inquires briskly as a theme with important carrying out immobilizing of the ionic conduction layer.

[0007] As a technique about the ion conductivity constituent of a non-fluidity, the polymer solid electrolyte which dissolved the salt is in polymers, such as polyethylene oxide. However, this polymer solid electrolyte is difficult for applying to a practical rechargeable lithium-ion battery, since ionic conduction resistance in ordinary temperature is now strong.

[0008] Moreover, there is a gel electrolyte which gelled the electrolytic solution used with a common rechargeable lithium-ion battery by the polymer as an immobilizing technique in which low ionic conduction resistance is realizable. The technique about the cell which used the separator and the gel electrolyte together is indicated by the U.S. Pat. No. 5,609,974 number. Moreover, the technique about a gel electrolyte cell in which the porous gel electrolyte was used like a separator is indicated by the U.S. Pat. No. 5,460,904 number. In this case, although a separator like a porosity film is not used, the gel film of the polyvinylidene fluoride system which held the electrolytic solution by the shape of porosity has structure which separates between two electrodes.

[0009]

[Problem(s) to be Solved by the Invention] However, although between two electrodes is separated by using a porous gel electrolyte like a separator with the technique indicated by the above-mentioned U.S. Pat. No. 5,460,904 number, when many electrolytes are made to contain by the inside of gel for the improvement in the cell engine performance, control of the distance between two electrodes is difficult, and there is a problem that the stable cell engine performance is not obtained.

[0010] Moreover, since the separator used as the hindrance of ionic conduction is contained as a component in invention indicated by the above-mentioned U.S. Pat. No. 5,609,974 number, ionic conduction resistance is strong. Thus, even if it replaces the electrolytic solution with a gel electrolyte with the structure of having the conventional separator using the electrolytic solution, the engine performance which is equal to the cell using a liquid electrolyte, i.e., the cell engine performance of the charge and discharge by the high current, has the problem of not being expectable.

[0011] Moreover, although the separator which does not contribute to ionic conduction which is used for the conventional cell is not used with the technique currently indicated by the above-mentioned U.S. Pat. No. 5,460,904 number, since the electrolytic solution which is not gelled inside [ of an electrode ] an active material layer and an ionic conduction layer exists, the problem that the consideration to the leakage of the electrolytic solution is needed is left behind.

[0012] It aims at offering the rechargeable battery with which the cell engine performance which is equal to the rechargeable lithium-ion battery which this invention solved the above problems, the separator which does not contribute to ionic conduction which is used from the former could control the distance between two electrodes to the precision, without using it, and did not need the consideration to a liquid spill, and used the conventional liquefied electrolyte is obtained.

[0013]

[Means for Solving the Problem] The 1st rechargeable battery concerning this invention is equipped with the ionic conduction layer which consists of an ion conductivity constituent containing the spacer particle which controls the distance of this positive-active-material layer and a negative-electrode active material layer of a non-fluidity between the positive electrode which formed the positive-active-material layer in the positive-electrode charge collector, the negative electrode which formed the negative-electrode active material layer in the negative-electrode charge collector, and the above-mentioned positive-active-material layer and a negative-electrode active material layer.

[0014] In the 1st rechargeable battery of the above, the mean particle diameter of a spacer particle of the 2nd rechargeable battery concerning this invention is 5 micrometers - 50 micrometers.

[0015] The 3rd rechargeable battery concerning this invention is distribution in which the particle size distribution of a spacer particle is included for 80% or more of all particles in the 0.3 times thru/or twice as many range of mean particle diameter as this in the 1st rechargeable battery of the above.

[0016] The 4th rechargeable battery concerning this invention has the spherical configuration of a spacer particle in the 1st rechargeable battery of the above.

[0017] The manufacture approach of the 1st rechargeable battery concerning this invention is equipped

with the process which produces the positive electrode and the negative electrode which formed the porous active material layer in the charge collector, the process which apply to one of active material layer front faces the mixed liquor of the above-mentioned positive electrode and a negative electrode which mixed the monomer and the spacer particle to the electrolytic solution, and the active material layer front face of the above-mentioned positive electrode and a negative electrode is made to counter them, and is laid on top of them at least, and the process which carries out the polymerization of the monomer in the condition piled up.

[0018] In the manufacture approach of the 1st rechargeable battery of the above, the mean particle diameter of a spacer particle of the manufacture approach of the 2nd rechargeable battery concerning this invention is 5 micrometers - 50 micrometers.

[0019] The manufacture approach of the 3rd rechargeable battery concerning this invention is distribution in which the particle size distribution of a spacer particle is included for 80% or more of all particles in the 0.3 times thru/or twice as many range of mean particle diameter as this in the manufacture approach of the 1st rechargeable battery of the above.

[0020] The manufacture approach of the 4th rechargeable battery concerning this invention is distribution in which the particle size distribution of a spacer particle is included for 80% or more of all particles in the 0.3 times thru/or twice as many range of mean particle diameter as this in the manufacture approach of the 1st rechargeable battery of the above.

[0021]

[Embodiment of the Invention] this invention persons use ion conductivity constituents of a non-fluidity, such as a gel electrolyte, for an ionic conduction layer. The separator which does not contribute to ionic conduction which is used from the former can control the distance between two electrodes to a precision, without using it. The result of having repeated research to the purpose which obtains the rechargeable battery with which the cell engine performance which is equal to the rechargeable lithium-ion battery which did not need the consideration to a liquid spill and used the conventional liquefied electrolyte is obtained, By the configuration in which the particle which has the suitable configuration which controls the distance between two electrodes, and magnitude in the ionic conduction layer which consists of an ion conductivity constituent of a non-fluidity is made to mix, it finds out that said purpose can be attained, and came to complete this invention.

[0022] Drawing 1 is the principal part cross section showing the gestalt of 1 operation of the rechargeable battery obtained by this invention, and shows the single electrode layered product. The positive-active-material layer by which 1 was formed in the positive-electrode charge collector, and 2 was formed on the positive-electrode charge collector 1 in drawing, The ionic conduction layer which consists of non-fluidity constituents, such as a negative-electrode active material layer by which 5 was formed in the negative-electrode charge collector, and 6 was formed on the negative-electrode charge collector 5, and a gel electrolyte with which 3 has been arranged between the positive-active-material layer 2 and the negative-electrode active material layer 6, 4 is a spacer particle which is mixed into the ionic conduction layer 3 and controls, the distance, i.e., the inter-electrode distance, between the positive-active-material layer 2 and the negative-electrode active material layer 6.

[0023] Although it is usable if it is a metal stable within a cell as the positive-electrode charge collector 1 used for the positive electrode and negative electrode concerning this invention, and a negative-electrode charge collector 5, copper is preferably used as aluminum and a negative-electrode charge collector 5 as a positive-electrode charge collector 1. Although anythings of the configuration of charge collectors 1 and 5, such as a foil, reticulated, and EKUSUPANDO metal, are usable, in order that what has large surface areas, such as reticulated and EKUSUPANDO metal, may obtain bond strength, it is used preferably.

[0024] As a positive-active-material layer 2 concerning this invention, what has the multiple oxide of transition metals, such as cobalt, manganese, and nickel, chalcogen compounds or these conjugated compounds, and various kinds of alloying elements is usable as an active material, without being limited. Moreover, as a negative-electrode active material layer 6, although a carbonaceous ingredient is used preferably, it can concern and use for chemical property in the cell of this invention. What has the

granular configuration of these active materials is used. The 0.3 to 20 micrometers thing of particle size is usable. Especially a 1 to 5 micrometers thing is desirable in respect of the dope of ion, such as a lithium ion at the time of charge and discharge, and dedope effectiveness. It becomes [ thin-film-izing of active material layers 2 and 6 is not easy, and / the irregularity of the front face of the active material layers 2 and 5 the pack density of an active material not only falls, but formed ] large and is not desirable when particle size is too large.

[0025] The spacer particle 4 used in order to control the distance between the positive-active-material layer 2 of a positive electrode and the negative-electrode active material layer 6 of a negative electrode (inter-electrode distance) is electronic insulation, and its stable ingredient is [ the ionic conduction layer 3 interior ] chemically usable. For example, rigid plastic particles, such as ceramics, such as an alumina, glass, a divinylbenzene system, and a polymethylmethacrylate system, can be used.

[0026] Although a fiber particle, a spherical particle, a scale-like particle, etc. can be used for the configuration of the spacer particle 4, from a homogeneous viewpoint of inter-electrode distance control nature, its spherical particle which does not have an anisotropy in particle shape is desirable.

[0027] Moreover, about particle size distribution, although the one where particle size distribution is narrower is desirable from a homogeneous viewpoint of inter-electrode distance control, if 80% or more of all particles are contained in the 0.3 times thru/or twice as many range of mean particle diameter as this, inter-electrode distance is controllable to satisfactory extent at homogeneity.

[0028] Moreover, since it cannot separate inter-electrode certainly about particle size if particle diameter is too small, 5 micrometers or more of mean particle diameter need to be 10 micrometers or more preferably. Moreover, since inter-electrode distance will become large beyond the need and ionic conduction resistance will increase if particle diameter is too large, it has a bad influence on the cell engine performance. As for this viewpoint to mean particle diameter, it is preferably desirable that it is 30 micrometers or less 50 micrometers or less.

[0029] As an ion conductivity constituent of a non-fluidity, the polymer solid electrolyte which dissolved lithium salt, the gel electrolyte which gelled the electrolytic solution by the polymer can be used for polymers, such as a polyethylene oxide system. From a viewpoint of making ionic conduction resistance low, a gel electrolyte is desirable. As the formation approach of this gel electrolyte, after mixing a monomer with the electrolytic solution, there are an approach which hardens by performing a polymerization, and a method of making the polymer which carried out the polymerization beforehand swell with the electrolytic solution, but since control of a presentation can be performed correctly and easily, it is desirable to use the former approach. Furthermore, a spacer particle is easily mixable into the ion conductivity constituent of a non-fluidity by adding the spacer particle for controlling inter-electrode distance into the liquid which mixed the monomer with the electrolytic solution, and carrying out a polymerization to it after that.

[0030] Although various things as a monomer for forming a gel electrolyte can be used, an acrylate monomer, a methacrylate monomer, etc. with an ethylene oxide chain are preferably used from the point of the holding power of good polymerization nature and an electrolyte. Moreover, the azobisisobutyronitril whose polymerization initiation by heat is attained as a polymerization initiator is usable.

[0031] As the electrolytic solution used in order to form a gel electrolyte, independent or the things which dissolved salts, such as  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ , and  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , in mixture, such as ethers solvents, such as dimethoxyethane, wood ether, and diethylether, polyethylene oxide of low molecular weight, ethylene carbonate, and propylene carbonate, can be used.

[0032] Below, as the single electrode layered product shown in drawing 1 is shown below, it is manufactured. The electrode which formed the porous negative-electrode active material layer 6 for the electrode in which the porous positive-active-material layer 1 was formed on the positive-electrode charge collector 1, on the negative-electrode charge collector 5 again is produced, respectively.

[0033] Production of each above-mentioned electrode applies and dries the positive-active-material paste and negative-electrode active material paste which mixed and adjusted positive active material and each negative-electrode active material to the solution which dissolved binder resin, such as

polyvinylidene fluoride, in solvents, such as N-methyl pyrrolidone (it abbreviates to NMP hereafter), on a positive-electrode charge collector and a negative-electrode charge collector, respectively, and rolls out and forms this in further predetermined thickness.

[0034] Apply the mixed liquor which mixed the spacer particle of particle size distribution the electrolytic solution, a monomer, and predetermined to the field of one of active material layers of the positive electrode of the produced electrode, and a negative electrode, the field of each active material layer is made to counter, and a polymerization is carried out with heating etc. in superposition and the condition of having pressurized. [ at least ] A monomer serves as a gel electrolyte by this polymerization, and it becomes a non-fluidity, and the problem of a liquid leak can control inter-electrode distance with a sufficient precision by the spacer particle while being lost.

[0035] Although the gestalt of the above-mentioned operation showed the example of the monolayer electrode mold cell which consists of a single electrode layered product which joined the positive electrode and the negative electrode to the field of the both sides of the ionic conduction layer 3, a positive electrode and a negative electrode can be arranged by turns among two or more ionic conduction layers, two or more electrode layered products may be formed, and cell capacity can be enlarged in proportion to an electrode layered product by having two or more electrode layered products.

[0036] Moreover, although the gestalt of the above-mentioned operation showed the rechargeable lithium-ion battery, this invention is applicable also to other rechargeable batteries by changing the class of active material, an electrolytic class, etc.

[0037]

[Example] Hereafter, an example explains this invention to a detail further.

Example 1

(Production of a positive electrode) The positive-active-material paste which adjusted LiCo2O by distributing 87 weight sections, the graphite powder 8 weight section, and the polyvinylidene fluoride 5 weight section to NMP It applied to thickness with a thickness of 200 micrometers with the doctor blade method on aluminium foil with a thickness of 20 micrometers, and this was left for 60 minutes in the 60-degree C dryer, it changed into the half-dry condition, and the positive electrode was produced by rolling out in thickness of 120 more micrometers. This positive electrode was cut to 5cmx4cm, and the terminal for current collection (tab) was attached in that edge.

[0038] (Production of a negative electrode) The negative-electrode active material paste which distributed and produced the mesophase-microbeads carbon (Osaka Gas make) 95 weight section and the polyvinylidene fluoride 5 weight section to NMP was applied to thickness with a thickness of 200 micrometers with the doctor blade method on copper foil with a thickness of 12 micrometers, and this was left for 60 minutes in the 60-degree C dryer, it changed into the half-dry condition, and the negative electrode was produced by rolling out in thickness of 120 more micrometers. This negative electrode was cut to 5cmx4cm, and the terminal for current collection (tab) was attached in that edge.

[0039] (Adjustment of a gel electrolyte mother liquor) As a monomer, 1 functionality monomer (GX-8301: Daiichi Pharmaceutical Co., Ltd. make) and 2 functionality monomer (PEM-1000: Daiichi Pharmaceutical Co., Ltd. make) were used.

[0040] as the electrolytic solution, the solution which dissolved LiPF<sub>6</sub> (Tokyo -- Formation -- make) in the mixed solution (it is 1:1 at a weight ratio) of ethylene carbonate (product made from Kanto Chemistry) and 1 and 2-dimethoxyethane (Wako Pure Chem make) by the concentration of 1.0 mol/dm<sup>3</sup> was used.

[0041] Azobisisobutyronitril (Tokyo formation Make) was used as a polymerization initiator.

[0042] As a spacer particle, the product made from a spherical alumina particle (CB-A20S: Showa Denko K.K.) was used. The mean particle diameter of this spherical alumina particle was 22 micrometers, and was the thing of the distribution included in the range 90% or more of whose particle is 15-30 micrometers.

[0043] 8% of the above-mentioned spacer particle was added by weight to the above-mentioned monomer, the electrolytic solution, and the mixed solution of a polymerization initiator, and the gel

electrolyte mother liquor of a presentation ratio shown in drawing 2 was produced.

[0044] (Production of a cell) The gel electrolyte mother liquor which carried out [ above-mentioned ] adjustment was applied to the active material layer front face of the above-mentioned positive electrode and each negative electrode, it inserted into the glass plate in the condition of having piled up so that both active material layers might counter further, the pressure of 10 g/cm<sup>2</sup> was put on the cell, it heated for 30 minutes at 80 degrees C, the polymerization of the monomer was carried out, and the cell was formed.

[0045] (Impedance measurement of a cell) The alternating current impedance of the produced cell was measured using the impedance analyzer (HYURETO Packard make, 4192A). The impedance of this cell was 0.51ohms.

[0046] (Short-circuit test) Where the produced cell is inserted monotonously, the impedance when putting a pressure on the whole cell was measured. The pressure was increased gradually, when the impedance changed rapidly, it judged that the short circuit arose, and the pressure value estimated the ease of carrying out of a short circuit. This cell produced the short circuit by the pressure of 0.5kg/cm<sup>2</sup> or more.

[0047] The positive electrode and negative electrode which were produced by the same approach as the example of comparison 1. above-mentioned example 1 are used. Mixed distribution of the spacer particle shown in the example 1 is carried out at the electrolytic solution which dissolved LiPF<sub>6</sub> (Tokyo -- Formation -- make) in the mixed solution (it is 1:1 at a weight ratio) of ethylene carbonate (product made from Kanto Chemistry), and 1 and 2-dimethoxyethane (Wako Pure Chem make) by the concentration of 1.0 mol/dm<sup>3</sup>. After having applied this suspension to the active material layer front face of two electrodes, making the active material layer side of two electrodes counter and piling up, it put between the glass plate by the pressure of 10 g/cm<sup>2</sup>, and the cell was produced.

[0048] Between two electrodes was in the condition which carried out the internal short circuit, and since this cell was this internal short circuit, it was not able to do charge and discharge.

[0049] The spherical alumina particle (B-A10: Showa Denko K.K. make) was used for the example 2. spacer particle, and others produced the cell like the above-mentioned example 1. The mean particle diameter of the spherical glass particle used by this example was 10 micrometers, and was the thing of the distribution included in the range 80% or more of whose particle is 3-20 micrometers. The configuration of the ingredient used for drawing 2 in this example is shown.

[0050] The impedance of this cell is 0.43ohms and produced the short circuit by the pressure of 0.1kg/cm<sup>2</sup> or more.

[0051] Using the spherical alumina particle (B-A05S: Showa Denko K.K. make) for the example of comparison 2. spacer particle, others produced the cell like the example 1. Mean particle diameter was 3 micrometers and this spacer particle was a diameter of a monodisperse particle contained in the range 90% or more of whose particle is 1-5 micrometers. The configuration of the ingredient used for drawing 2 in this example of a comparison is shown.

[0052] Between two electrodes was in the condition which carried out the internal short circuit, and since this cell was this internal short circuit, it was not able to do charge and discharge.

[0053] The spherical alumina particle (CB-A30S: Showa Denko K.K. make) was used for the example 3. spacer particle, and others produced the cell like the above-mentioned example 1. The mean particle diameter of the spherical alumina particle used by this example was 29 micrometers, and was the thing of the distribution included in the range 90% or more of whose particle is 20-40 micrometers. The configuration of the ingredient used for drawing 2 in this example is shown.

[0054] The impedance of this cell is 0.81ohms and produced the short circuit by the pressure of 0.6kg/cm<sup>2</sup> or more.

[0055] Using the spherical alumina particle (A-13H, Showa Denko K.K. make) with a mean particle diameter of 55 micrometers for the example of comparison 3. spacer particle, others produced the cell like the example 1. The configuration of the ingredient used for drawing 2 in this example of a comparison is shown.

[0056] The impedance of this cell is 1.25ohms and produced the short circuit by the pressure of



0.8kg/cm<sup>2</sup> or more.

[0057] Others produced the cell like the example 1 using what carried out tales-doses mixing of the thing (the mean particle diameter of 10 micrometers, 22 micrometers, and 29 micrometers) used for the example 4. spacer particle by the above-mentioned example 1 thru/or 3 by the weight ratio. The configuration of the ingredient used for drawing 2 in this example is shown.

[0058] The impedance of this cell is 0.75ohms and produced the short circuit by the pressure of 0.2kg/cm<sup>2</sup> or more.

[0059] In this example, since three kinds of spacer particles were mixed, the particle size distribution of a spacer particle became a little large, therefore control of inter-electrode distance became incorrectness a little, it is thought that the impedance became a little large and it changed into the condition that a short circuit also tends [ a little ] to take place.

[0060] Using the spacer particle shown in the example 5. above-mentioned example 1, the amount of the spacer particle to the mixed solution in a gel electrolyte mother liquor was increased to 16% of the weight, and others produced the cell like the example 1. The configuration of the ingredient used for drawing 2 in this example is shown.

[0061] The impedance of this cell is 0.62ohms and produced the short circuit by the pressure of 0.8kg/cm<sup>2</sup> or more.

[0062] Using the spacer particle shown in the example of comparison 4. above-mentioned example 1, the amount of the spacer particle to the mixed solution in a gel electrolyte mother liquor was increased to 50% of the weight, and others produced the cell like the example 1. The configuration of the ingredient used for drawing 2 in this example of a comparison is shown.

[0063] The impedance of this cell is 1.07ohms and produced the short circuit by the pressure of 1.0kg/cm<sup>2</sup> or more.

[0064] Using the spacer particle shown in the example 6. above-mentioned example 1, the amount of the spacer particle to the mixed solution in a gel electrolyte mother liquor was reduced to 4% of the weight, and others produced the cell like the example 1. The configuration of the ingredient used for drawing 2 in this example is shown.

[0065] The impedance of this cell is 0.47ohms and produced the short circuit by the pressure of 0.2kg/cm<sup>2</sup> or more.

[0066] Using the spacer particle shown in the example of comparison 5. above-mentioned example 1, the amount of the spacer particle to the mixed solution in a gel electrolyte mother liquor was reduced to 1.0% of the weight, and others produced the cell like the example 1. The configuration of the ingredient used for drawing 2 in this example of a comparison is shown.

[0067] Between two electrodes was in the condition which carried out the internal short circuit, and since this cell was this internal short circuit, it was not able to do charge and discharge.

[0068] Increasing the amount of the monomer for forming an example 7. gel electrolyte, others produced the cell like the example 1. The configuration of the ingredient used for drawing 2 in this example is shown.

[0069] The impedance of this cell is 1.3ohms and produced the short circuit by the pressure of 0.9kg/cm<sup>2</sup> or more.

[0070] Reducing the amount of the monomer for forming an example 8. gel electrolyte, others produced the cell like the example 1. The configuration of the ingredient used for drawing 2 in this example is shown.

[0071] The impedance of this cell is 0.4ohms and produced the short circuit by the pressure of 0.1kg/cm<sup>2</sup> or more.

[0072] Using inorganic whisker-like powder (KaowoolBulk1260 middle) for the example of comparison 6. spacer particle, others produced the cell like the example 1. The diameter of average fiber was [ 4 micrometers and the mean fiber length of this spacer particle ] 19 micrometers. The configuration of the ingredient used for drawing 2 in this example of a comparison is shown.

[0073] The impedance of this cell is 0.68ohms and produced the short circuit by the pressure of 0.1kg/cm<sup>2</sup> or more.



[0074] In this example of a comparison, since there was an anisotropy in a configuration at the shape of a fiber with a big spacer particle and dispersion in spacing arose with the location of two electrodes, it is thought that the impedance became large.

[0075] Using the alumina (AS-20, Showa Denko K.K. make) for the example of comparison 7. spacer particle, others produced the cell like the example 1. Although the mean particle diameter of this spacer particle was 20 micrometers, that configuration was a thing roundish [ wore ]. The configuration of the ingredient used for drawing 2 in this example of a comparison is shown.

[0076] The impedance of this cell is 0.64ohms and produced the short circuit by the pressure of 0.2kg/cm<sup>2</sup> or more.

[0077] Since the configuration of the spacer particle used for this example of a comparison is an indeterminate form, a little, an impedance becomes large and is considered that a short circuit also becomes easy to take place.

[0078] It considered as the structure which puts between inter-electrode the polyolefine system separator film (trade name: Celgard #200, Hoechst A.G. make) currently widely used for the rechargeable lithium-ion battery instead of the example of comparison 8. spacer particle, and inter-electrode was filled up with the gel electrolyte (a spacer particle is not mixed) used in the example 1, and the cell was formed.

[0079] The impedance of this cell was 1.2ohms and its resistance was high compared with the cell which controlled inter-electrode using the spacer particle. Moreover, even if this cell put the pressure of 1.0kg/cm<sup>2</sup>, it was not short-circuited.

[0080] It is in \*\* to be shown below from the above-mentioned example and the example of a comparison. According to the example 1, by using the ionic conduction layer which consists of a polymer containing a spacer particle by which immobilizing was carried out shows that control an inter-electrode distance with a sufficient precision, without using the separator constituting the cause of increase of ionic conduction resistance, and the problem of a liquid leak is solved. With the structure which, on the other hand, combined the liquid electrolyte shown in the example 1 of a comparison, and the spacer particle, distance between two electrodes cannot be kept certain. That is, to control the distance between two electrodes by the spacer particle, to combine with the electrolyte of a non-fluidity is required.

[0081] Although the distance between two electrodes becomes small and becomes the inclination which is a little easy to short-circuit as a result like an example 2 when what has a little small particle diameter of a spacer particle is used, ionic conduction resistance can be decreased. In the example 2 of a comparison, since the particle diameter of a spacer particle was too small, distance between two electrodes could not be maintained, and a short circuit was not able to be prevented. These results show that it is required to be 5 micrometers or more as mean particle diameter of a spacer particle.

[0082] Although it becomes possible like an example 3 for the distance between two electrodes to become large, consequently to prevent a short circuit more effectively when what has a little large particle diameter of a spacer particle is used, ionic conduction resistance increases a little by one side. In the example 3 of a comparison, since the particle diameter of a spacer particle is too large, the distance between two electrodes becomes large too much, and ionic conduction resistance becomes extremely high. These results show that it is required to be 50 micrometers or less as mean particle diameter of a spacer particle.

[0083] An example 4 mixes the spacer particle from which particle diameter differs, and although it is the example which extended particle size distribution, if the particle size distribution of a spacer particle spreads, while the function to hold the distance between two electrodes and to prevent a short circuit will fall, ionic conduction resistance also increases. Therefore, although the narrower one of the particle size distribution of a spacer particle is desirable, particle size distribution is understood that it is required for the 0.3 times thru/or twice as many range of mean particle diameter as this to contain 80% or more of all particles from the result of the above-mentioned example.

[0084] Although a short circuit can be prevented more effectively and can be used as a reliable cell if the amount of a spacer particle is made [ many ] like an example 5, ionic conduction resistance increases. Like the example 4 of a comparison, if there are too many amounts of a spacer particle, ionic conduction

resistance will increase extremely. Moreover, although it is in the inclination which a little becomes easy to short-circuit like an example 6 when the amount of a spacer particle is lessened, ionic conduction resistance can be decreased. If there are too few amounts of a spacer particle like the example 5 of a comparison, the result that the short circuit has already arisen in the phase which forms a cell will be brought.

[0085] Moreover, although a short circuit can be prevented more effectively and it can consider as a reliable cell if the content of the polymer in an ionic conduction layer increases like an example 7, ionic conduction resistance increases. Moreover, although ionic conduction resistance will fall if the content of the polymer in an ionic conduction layer decreases like an example 8, a short circuit arises by the lower pressure.

[0086] Therefore, it becomes possible to be wide range and to control a cell property like the design which gave priority to dependability the amount of a polymer, the amount of a spacer particle, and by setting up the particle diameter of a spacer particle appropriately further, and the design which gave priority to the cell engine performance, from control of ionic conduction resistance and inter-electrode distance, and a viewpoint of maintenance.

[0087]

[Effect of the Invention] According to invention concerning claims 1 and 5, the 1st rechargeable battery Between the positive electrode which formed the positive-active-material layer in the positive-electrode charge collector, the negative electrode which formed the negative-electrode active material layer in the negative-electrode charge collector, and the above-mentioned positive-active-material layer and a negative-electrode active material layer It has the ionic conduction layer which consists of an ion conductivity constituent containing the spacer particle which controls the distance of this positive-active-material layer and a negative-electrode active material layer of a non-fluidity. By things An inter-electrode distance is controlled with a sufficient precision, without using the separator constituting the cause of increase of ionic conduction resistance, and the problem of a liquid leak is solved, and it is effective in the rechargeable battery of high performance being obtained.

[0088] While improving the ionic conduction of an ionic conduction layer by setting mean particle diameter of a spacer particle to 5 micrometers - 50 micrometers according to invention concerning claims 2 and 6, control of an accurate inter-electrode distance can be performed and a short circuit can be effectively controlled by maintenance of the distance.

[0089] According to invention concerning claims 3 and 7, by considering particle size distribution of a spacer particle as the distribution in which 80% or more of all particles are contained in the 0.3 times thru/or twice as many range of mean particle diameter as this, control of an accurate inter-electrode distance can be performed and a short circuit can be effectively controlled by maintenance of the distance.

[0090] According to invention concerning claims 4 and 8, by making the configuration of a spacer particle spherical, control of an accurate inter-electrode distance can be performed and a short circuit can be effectively controlled by maintenance of the distance.

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[Translation done.]